Molecular Weight Determination of Pyrrole-based Polymers

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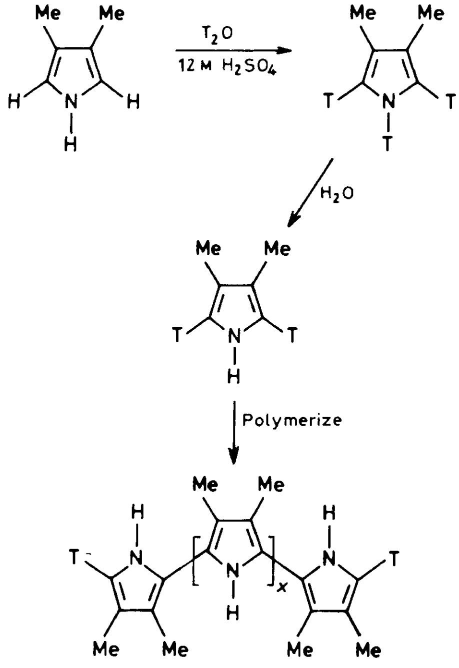
The first molecular weight determination for a pyrrole based conducting polymer indicates that poly(β,β′-dimethylpyrrole) consists of chains of up to *ca.* 1000 pyrrole units.

The electrical properties of polymers based on pyrroles are of interest not only for their attractive physical properties, particularly their stability but also because these polymers are the first to show experimental evidence for the role of bipolarons in their transport properties.[1-4] The molecular weight is a key parameter both in determining the physical properties of these polymers and to the theories of conduction in such systems, however the insolubility of all such polymers prevents the use of standard techniques for measurement of molecular weight.

The molecular weight determination reported here is based on the assumption that the polymerization proceeds by coupling of the electrochemically produced radical cations of the monomer *via* the α-carbon atoms, followed by the elimination of an α-proton to give a polymer in which all the protons in the α-positions are eliminated except for those on the terminal pyrroles.[5] The concentration of terminal protons can then be used to obtain the polymer chain length. This concentration can be accurately determined by radiochemical techniques using a pyrrole labelled with tritium in the α-position.

The technique is particularly appropriate for the determination of the molecular weight of β,β′-dimethylpyrrole polymers because the absence of β-hydrogens ensures that the bonding along the chain is exclusively *via* the α,α′-carbon atoms[5,6] and that the tritium labelling is only in the α-positions of the monomer. The monomer was labelled by tritiating the three ring hydrogens with 12 M H_2SO_4–T_2O and then removing the tritium on the nitrogen atom by washing with H_2O (Scheme 1). The films of poly(dimethylpyrrole) were grown electrochemically on platinum electrodes in acetonitrile solutions using silver perchlorate or tetrafluoroborate as the electrolyte.[5] A two electrode, single compartment cell was used and the films were grown at a constant potential of 0.125 V for *ca.* 2 h. The films were then combusted in oxygen, the water produced collected and the amount of tritium present determined by standard techniques. From a comparison of the amount of tritium remaining with the amount of tritium present



Scheme 1

originally in the monomer, the average number of repeat units in the polymer was determined.

This ratio could be distorted by any significant exchange of tritium between the solvent and the pyrrole monomer or the pyrrole polymer. Exchange is known to take place very readily at the pyrrole nitrogen atom but this problem was easily eliminated by removing the tritium from the polypyrrole nitrogen atoms by repeated washing. Exchange at the other positions in the monomer takes place only under much stronger acid conditions than used in the experiment. The absence of exchange at the α-carbon atom of the monomer under the conditions of film growth was demonstrated by dissolving dimethylpyrrole in deuteriated acetonitrile and observing from n.m.r. studies that no deuterium exchange took place over a period of time long compared with that of the experiment. We also confirmed that exchange of tritium with the polymer does not take place. This was established by taking a sample of the tritiated polymer film and dividing it into two parts. The first part was washed several times to remove the electrolyte and to exchange the protons on the nitrogen atom, while the second was soaked in acetonitrile for one week. The activity of both films was then compared and found to be essentially the same, indicating no exchange takes place.

The results showed that the average number of pyrrole units in films grown as described was about 750 for the poly(dimethylpyrrole) perchlorate which corresponds to a molecular weight of about 100 000. In the case of the poly(dimethylpyrrole) tetrafluoroborate grown under identical conditions the molecular weight was about 50 000. By varying the growth conditions, polymers can be obtained with molecular weights 10 000—125 000. If during the polymerization process the proton is not eliminated from the α-carbon atom, an sp^3 bond will be formed which will force the chain out of planarity and terminate the sequence of conjugation. Thus the number of repeat units given above for the molecular weight will under these circumstances more accurately represent the number of pyrrole units in uninterrupted conjugated sequences on the chains and the molecular weight will be higher than estimated. Similarly if crosslinking exists, the molecular weight will be higher than estimated. These numbers therefore should be taken as minimum values for the molecular weight of poly(dimethylpyrrole). Thus the molecular weight of the poly(dimethylpyrrole) is quite substantial, certainly large enough to support bipolarons. However the molecular weight of polypyrrole itself may be significantly different in view of the potential role of the β-carbon atoms in chain branching.[7] Estimates of the chain length of polypyrrole can be made by assuming that excess of hydrogen is present only in terminal pyrroles. This leads to chains of 6—8 pyrrole units which seems too small in view of the properties of the polymer. Yakushi *et al.*[8] have concluded that polypyrrole has a wide range of chain lengths including some very short oligomers.

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